

**Disclaimer:**

This English translation is produced by machine translation and may contain errors. The JPO, the INPIT, and those who drafted this document in the original language are not responsible for the result of the translation.

**Notes:**

1. Untranslatable words are replaced with asterisks (\*).
2. Texts in the figures are not translated and shown as is.

Translated: 06:04:23 JST 07/08/2011

Dictionary: Last updated 06/10/2011 / Priority:

---

**FULL CONTENTS**

---

**[Claim(s)]**

[Claim 1]An epoxy resin constituent characterized by porosity resin particles containing one to 80 weight section to epoxy resin 100 weight section.

[Claim 2]The epoxy resin constituent according to claim 1 whose porosity resin particle is 1-20 micrometers of number mean particle size, and BET specific surface area 1-30m<sup>2</sup>/g.

[Claim 3]The epoxy resin constituent according to claim 1 to 2 characterized by ratios of a volume mean particle size to a number mean particle size being 1.0-1.3 in a mean particle size of porosity resin particles.

[Claim 4]The epoxy resin constituent according to claim 1 to 3 whose porosity resin particle is polyamide.

---

**[Detailed Description of the Invention]**

[0001]

[Field of the Invention][The technical field which carries out an invention]. It is related with the epoxy resin which distributed porosity resin particles, and excels in processability, such as thixotropy, and this inventions are compatibility and adhesion \*\*\*\*\*.

It excels in \*\*\*\* and hardness and they are a paint, adhesives, a sealing agent, and other electronic industry materials.

[0002]

[Description of the Prior Art]As for the epoxy resin, an electric insulation material, a laminate sheet, engineering works and construction, a paint, adhesives, etc. are used broadly industrially. The inorganic filler is blended for improvement in heat resistance and an electrical

property. However, there is a tendency for shock resistance, heat-resistant shock nature, etc. to get worse, by adding an inorganic filler. Therefore, for example, the method of impregnating with and adding a functional group content diene system polymer on an inorganic powder object is indicated (JP,H5-39409,A).

[0003]JP,2000-72986,A has disclosed in order to improve thermal shock nature, blend core shell type thermoplastics and liquid rubber. However, since these are using the rubber-like thing as the ingredient, they may be inferior in mechanical properties, such as hardness.

[0004]moreover -- JP,H11-323202,A -- cyclamate -- being related with the powdered paint for giving TOROPI nature is indicated. However, handling had the problem of being difficult, from the CHIKUSOTOROPI grant agent consisting of fine particles.

[0005]

[Problem to be solved by the invention]The purpose of this invention is to provide the epoxy resin constituent which was excellent in the processability of excelling in thixotropy and excelling in handlability, and was excellent in mechanical properties, such as the destructive characteristics, such as compatibility, shock resistance, and hardness.

[0006]

[Means for solving problem]This invention relates to an epoxy resin constituent, wherein porosity resin particles contain one to 80 weight section to epoxy resin 100 weight section.

[0007] As for this invention, it is preferred that porosity resin particles are 1-20 micrometers of number mean particle size and BET specific surface area 1-30m<sup>2</sup>/g.

[0008]As for this invention, in the mean particle size of porosity resin particles, it is preferred that the ratios of a volume mean particle size are 1.0-1.3 to a number mean particle size.

[0009]As for this invention, it is preferred that porosity particles are polyamide. Hereafter, this invention is explained in detail.

[0010]

[Mode for carrying out the invention]The epoxy resin of this invention has an epoxy group in a molecule chain, and specifically, Glycidyl ether system epoxy resins, such as a bisphenol A type epoxy resin, a screw phenol F type epoxy resin, a bisphenol A D type epoxy resin, a novolac type epoxy resin, and a bromination epoxy resin, are made into the start, Phthalic acid diglycidyl ester, tetrahydrophthalic acid diglycidyl ester, diglycidyl hexahydrophthalate, diglycidyl p-oxybenzoic acid, dimer acid diglycidyl ester, the diglycidyl cyclopentane 1, Glycidyl ester system epoxy resins, such as 3-dicarboxylate, Glycidyl amine system epoxy resins, such as N and N-diglycidyl aniline, tetraglycidyl ether JIAMINO diphenyl methane, triglycidyl p-amino phenol, tetraglycidyl ether KISHIRI range amine, and tetraglycidyl ether screw aminomethyl cyclohexane, Hydantoin type epoxy resins, such as ring type fatty series epoxy resin [ which has a cyclohexene oxide machine, a tricyclo decene oxide machine and a cyclo pen ten oxide machine ], 1, and 3-diglycidyl hydantoin, triglycidyl isocyanurate, Epoxidation poly butadiene

etc. are mentioned. Also in these, the epoxy resin of the epoxy equivalents 150-5000 is preferred. In this invention, it can also be used combining two or more sorts of epoxy resins. [0011]The epoxy resin constituent of this invention can add a hardening agent and a hardening accelerator. As a hardening agent, an acid anhydride, amine, phenol, imidazole derivatives, etc. are mentioned, for example. As a hardening accelerator, hardening accelerators, such as salts with tertiary amine, imidazole derivatives, amide, a diaza compound, polyvalent carboxylic acid, phosphinic acid, and phenol, etc. can be mentioned.

[0012]As an acid anhydride, for example A phthalic acid anhydride, a trimellitic acid anhydride, A pyromellitic acid anhydride, a benzophenone tetracarboxylic acid anhydride, ethylene glycol trimellitic anhydride, Aromatic-carboxylic-acid anhydrides, such as a biphenyl tetracarboxylic acid anhydride, azelaic acid, Alicyclic carboxylic anhydrides, such as the anhydride of aliphatic carboxylic acid, such as sebacic acid and DODEKAN 2 acid, a tetrahydrophthalic anhydride, a hexahydrophthalic anhydride, a NAJIKKU acid anhydride, a beef fat acid anhydride, and himic acid anhydride, are mentioned.

[0013]As amine, they are mentioned by JIAMINO diphenyl methane, JIAMINO diphenylsulfone, JIAMINO diphenyl ether, etc., for example, and, [ as phenol ] For example, bisphenol A, tetra-BUROMU bisphenol A, screw phenol F. A - biphenyl phenol, and screw phenol S, 4, and 4 '2, 2'-methylene screw (4-methyl 6-tert-butylphenol), A 2 and 2'-methylene screw (4-ethyl 6-tert-butylphenol), 4,4'-butyrylene-bis(3-methyl-6-tert-butylphenol), 1, 1, 3-tris (2-methyl 4-hydroxy 5-tert-butylphenol), Tris hydroxyphenyl methane, pyrogallol, the phenol that have a diisopropylidene skeleton, The phenol which has fluorene skeletons, such as 1 and 1-G 4-hydroxyphenyl full OREN, Polyphenol compounds, such as phenol-ized poly butadiene, phenol, cresol, ethylphenol, butylphenol, octyl phenol, bisphenol A, Blom-ized bisphenol A, the screw phenol F, the screw phenol S. Various novolac resin, such as novolac resin which uses various phenol system compounds, such as naphthols, as materials, KISHIIRIEN frame content phenol novolac resin, dicyclopentadiene frame content phenol novolac resin, and fluorene skeleton content phenol novolac resin, is mentioned.

[0014]As imidazole derivatives, for example 2-methyl imidazole, 2-phenyl imidazole, 2-UNDESHIRU imidazole, 2-heptadecyl imidazole, 2-phenyl 4-methyl imidazole, 1-benzoroux 2-phenyl imidazole, 1-benzoroux 2-methyl imidazole, 1-cyano ethyl 2-methyl imidazole, 1-cyano ethyl 2-phenyl imidazole, 1-cyano ethyl 2-UNDESHIRU imidazole, 2, 4-Gia Minaux 6 (2'-methyl imidazole (1')) ethyl s-triazine, 2, 4-Gia Minaux 6 (2'-UNDESHIRU imidazole (1')) ethyl s-triazine, 2, 4-Gia Minaux 6 (2'-ethyl, 4-methyl imidazole (1')) ethyl s-triazine, 2, a 4-Gia Minaux 6 (2'-methyl imidazole (1')) ethyl s-triazine isocyanuric acid addition, 2:3 additions of 2-methyl imidazole isocyanuric acid, 2-phenyl imidazole isocyanuric acid addition, the 2-phenyl 3, 5-dihydroxy methyl imidazole, 2-phenyl 4-hydroxymethyl 5-methyl imidazole, The 1-cyano ethyl 2-phenyl 3, the various imidazole derivatives of 5-dicyano ethoxymethyl imidazole, And salts

with polyvalent carboxylic acid, such as these imidazole derivatives, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, NAFTA range carboxylic acid, maleic acid, and oxalic acid, are mentioned.

[0015]As a hardening accelerator, those, such as dicyandiamide, 1, 8-diaza bicyclo (5.4.0) undecene 7, bird phenyl phosphine, tetra-phenyl phosphonium tetraphenylborate, 2 and 4, and 6-tris aminomethyl phenol, is mentioned, for example.

[0016]This invention is a resin particle restoration epoxy resin constituent characterized by porosity resin particles containing one to 80 weight section to epoxy resin 100 weight section. Porosity resin particles are one to 70 weight sections preferably. To epoxy resin constituent 100 weight section, if there are few combination rates of porous resin particles than one weight section, the effect of particle addition will decrease. Since it will become impossible for an epoxy resin to form a matrix enough, and uniform mechanical properties are not revealed, it is [ be / it / if / resin particles are larger than 80 weight sections, ] inconvenient.

[0017]The porosity resin particles of this invention are particles which the specific surface area is larger than the specific surface area of the same diameter of a particle with the smooth surface, and have unevenness in a particle surface. If an epoxy resin is filled up with the porosity resin particles of this invention, they will give a thixotropic action to an epoxy resin in the case of processing. the time of being used as a paint or adhesives by doing so -- liquid -- whose generating is prevented and shape holdout becomes good.

[0018]They are 1-20 micrometers of number mean particle sizes of the porosity resin particles of this invention. 2-15 micrometers is preferably preferred. If smaller than the mean diameter of 1 micrometer, handling will worsen. When the number mean diameter was larger than 20 micrometers and it uses for a paint or adhesives, the CHIKUSOTOROPI effect may fall and it is not desirable.

[0019]The specific surface area according [ the porosity resin particles of this invention ] to a BET adsorption process is  $1\text{-}30\text{m}^2/\text{g}$ . It is  $2\text{-}20\text{m}^2/\text{g}$  preferably. If specific surface area is smaller than  $1\text{m}^2/\text{g}$ , the CHIKUSOTOROPI effect will fall. It is it hard to treat that specific surface area is  $30\text{m}^2/\text{g}$ , and handling worsens. The above-mentioned range of the diameter of a particle and specific surface area of porous resin particles is preferred.

[0020]Distribution of this porosity resin particle of this invention is uniform diameter distribution of a particle whose ratios (PDI) of the volume mean particle size (Dv) to the number mean particle size (Dn) are 1.0-1.3. Preferably, the ratio is 1.0-1.2. If the ratio of the volume mean particle size to a number mean particle size is larger than 1.3, distribution of the diameter of a particle is too large, and since the surface property of an epoxy resin constituent, processability, etc. may be spoiled, it is not desirable.

[0021]The porous resin particles of this invention are crystalline resin particles, such as

polyamide, polyester, and polyimide. Polyamide is preferably preferred. The melting point of polyamide is 110-320 °C. Preferably, it is 140-280 °C. Publicly known various things can be mentioned as polyamide used by this invention. For example, it is obtained by heavy condensation of cyclic amide or dicarboxylic acid, and *Gia Min*. As a monomer, epsilon-caprolactam, epsilon-aminocaproic acid, omega-RAURO lactam, The crystalline polyamide produced by polymerizing cyclic amide, such as omega-amino dodecanoic acid and omega-amino undecanoic acid, Oxalic acid, adipic acid, sebacic acid, terephthalic acid, isophthalic acid, It is obtained by carrying out heavy condensation of *Gia Min*, such as dicarboxylic acid, such as 1,4-cyclohexyl dicarboxylic acid, ethylene diamine, hexamethylenediamine, 1,4-cyclohexyl JIAMIN and m-KISHIRI range amine, pentamethylene JIAMIN, and decamethylene JIAMIN.

[0022]The crystalline polyamide etc. which the crystalline polyamide of this invention turns into from independent polymers and these copolymers are mentioned. Specifically, they are the polyamide 6, the polyamide 66, the polyamide 11, the polyamide 12, the polyamide 610, the polyamide 66/6T (T expresses a terephthalic acid ingredient), etc. It may be a mixture of the above-mentioned polyamide. The polyamide 6, the polyamide 66, the polyamide 11, and the polyamide 12 are preferred especially preferably.

[0023]The molecular weights of the polyamide of this invention are 2,000-100,000. It is 5,000-40,000 preferably.

[0024]The manufacturing method of the polyamide porosity particles of uniform particle diameter of this invention is described. After forming uniform solution temporarily by mixing the non-solvent of polyamide, and water with the aromatic alcohol system solution of polyamide, porosity particles can be obtained by depositing polymer.

[0025]0.1 to 30 weight % and an aromatic alcohol system solvent are 99.8 to 70 weight %, and polyamide of a polyamide solution is a total of 100weight %. Preferably, polyamide is 0.2 to 25 weight %.

[0026][0027] with 0-cresol, m-cresol, p-cresol, chlorophenol, etc. preferred as a solvent of the aromatic alcohol system solution used for a polyamide solution The non-solvent of polyamide has that preferred in which an aromatic alcohol system solvent and water carry out compatible partially at least. Alcohol, ketone, etc. are preferred. It is important for water to carry out compatible. For example, methanol, ethanol, propanol, acetone, etc. are preferred.

[0028]The rate of the sum total of the non-solvent and water of the non-solvent of polyamide is that polymer fluid is comparatively more large.

[0029]The rate of water of weight % of the non-solvent and water of polyamide is 2 to 90 weight % to a total of 100 weight %. In that case, an addition order of solution may add a polyamide non-solvent to a polyamide solution, and then may add water to it. Or polymer fluid may be added after mixing water with a polyamide non-solvent. After mixing \*\*\*\* to a

polyamide solution, polyamide non-\*\*\*\*\* may be added. After mixing water with a polyamide non-solvent, it is preferred to add polymer fluid. Any method may be used as long as \*\* 1 which is solution is maintained.

[0030]It is important for each rate of the polyamide solution of this invention, a polyamide non-solvent, and water that three persons become a compatible system. Uniform solution is made to form, time progress is obtained, and polymer particles are deposited. Time to form uniform solution is the time for 0.1 second - about 120 minutes, for example. It is important to form uniform solution also temporarily. if required -- suitable churning -- also adding -- it is good.

[0031]As for the temperature which deposits polymer particles from this 3 ingredient solution, 10-60 \*\* is preferred. The solvent composition range where solution becomes uniform depending on temperature may become large. If lower than the temperature of 10 \*\*, the becoming uniform field may become narrow. If higher than the temperature of 60 \*\*, the steam pressure of a solvent becomes high and is not preferred.

[0032]The polyamide particles which deposited by this invention can be isolated from solution by the usual methods, such as DEKANTESHON, centrifugal separation, and filtration. For example, the liquid which \*\*\*\*(ed) polyamide particles may be further diluted and centrifuged with methanol. Methanol may wash several times and centrifugal separation may be repeated. Next, hot air drying and vacuum drying may be presented.

[0033]Thus, the manufactured polymer particles turn into porosity polyamide particles of uniform particle diameter. For example, the umbrella density of 0.1-0.4 g/cm<sup>3</sup> is 0.2-0.3 g/cm<sup>3</sup> preferably in the uniform diameter of a particle of 1-20 micrometers of particle diameter. BET specific surface area 1-30m<sup>2</sup>/g -- it is preferably set to 2 - 20 m<sup>2</sup>/g. They are the diameters 2-15micro of a particle preferably.

[0034]The porous resin particle restoration epoxy resin constituent of this invention can be manufactured as follows, for example. For example, an epoxy resin, porosity resin particles, a hardening agent, a hardening accelerator, a bulking agent, etc. Combination ingredients, such as a coupling agent, fire retardant, colorant, a leveling agent, and lubricant, using the Henschel mixer etc. with a kneader, an extruder, etc., [ after dry blending ] For example, after performing a melting mixing process below 110 \*\*, it is good also as an epoxy resin constituent of this invention to carry out cooling solidification and carry out the after [ fine pulverization ] part class of the mixture.

[0035]Dissolve an epoxy resin in a solvent, dissolve or distribute porosity resin particles and a required additive agent in epoxy resin solution by a wet type, if necessary, will heat, and a solvent is distilled off, After performing a mixing process by kneader, an extruder, etc., it is good also as an epoxy resin constituent of this invention to carry out cooling solidification and carry out the after [ fine pulverization ] part class of the mixture. In that case, as a solvent, if an epoxy resin dissolves, it will not limit, but acetone, methyl ethyl ketone, toluene, a tetrahydro

franc, chloroform, etc. are preferred.

[0036]The porosity resin particle particle restoration epoxy resin constituent of this invention is a range which does not have influence in the feature of an invention in addition to this, and may add additives, such as an antioxidant, processing aid, a dispersing agent, and a filler, thermoplastics, thermosetting resin, or liquefied resin.

[0037]Since porosity resin particles are distributed as a filler, the porosity resin particle restoration epoxy resin of this invention is excellent in the impact fracture-proof characteristic, the crack destructive characteristic, and the fracture characteristic excellent in destructive intensity. Stress is easy to be distributed for porosity particles, and a micro crack can guess that growth of a crack is prevented. Since this invention is a porosity bulking agent, thixotropy reveals it preferably.

[0038]Since this invention is a porosity resin particle restoration epoxy resin. [ in the case of processing ] It is preferably given by thixotropy and, [ after hardening ] As a filler which excels [ particles / porosity ] in moderate reinforcement nature, the impact fracture-proof characteristic, From excelling in destructive intensity, such as crack-proof growth possibility, it seems that an epoxy resin suitable for the use of the packing of the machinery field, a paint, adhesives, and the electronics field, a gasket, housing, a pad, a board, a connector, an adapter, etc. can be provided.

[0039]

[Working example]Hereafter, although an working example explains this invention concretely, this invention is not limited to these working examples. The examination and valuation method, or judging standard in an working example and a comparative example is as being shown below.

[0040]It observed with the measuring method and the valuation method (mean particle size) scanning electron microscope, and observed as particle shape and a size. Globular form particles read particle diameter. All computed 100 number mean particle sizes and volume mean particle sizes. The following formula was used.

: Number mean particle size : [Mathematical formula 1]

$$Dn = \sum_{i=1}^n Xi / n$$

Volume mean particle size: [Mathematical formula 2]

$$Dv = \sum_{i=1}^n Xi^4 / \sum_{i=1}^n Xi^3$$

Particle-size-distribution index: PDI=Dv/Dn [0041] (Specific surface area) It measured by the one BET specific surface area method.

[0042](Thixotropy) Inclination flow nature was made into the thixotropic measure. The tablet

with a 0.5g balance picking and a diameter [  $\phi$  ] of 10 mm was tableted for the powdered paint, the tablet was put on the inclination board of 60 angles of inclination under 150 \*\* atmosphere, and the distance into which the tablet of 3 minutes after carried out melting, and flowed was measured with slide calipers.

[0043](Heat-resistant shock nature) After applying the sample to a thickness of 500 micrometers and making it harden in 150 \*\* 1 hour, the cycle test was done in 120 \*\*, 30 minutes, -40 \*\*, and 30 minutes, and crack generating was measured. It expressed with the number of times of a cycle which the crack generated in the paint thing.

[0044](Hardness) Pencil hardness was measured according to JIS K5400.

[0045](Reference example 1) Manufacture polyamide 6 (molecular weight 13,000) of polyamide porosity particles was used as 14.3 weight % of 5.0 weight % of concentration m-cresol solution, and 14.3 weight % of water was mixed with 71.4 weight % of methanol, and it added, agitating to a polyamide solution. Solution became uniform after 1-minute churning. Polymer has deposited in 2 minutes from the bottom of churning. It settled for 24 hours and the deposit was terminated. Polymer was isolated by centrifugal separation after that. When observed with the scanning electron microscope, they were a number average diameter of 7.81 micrometers, 8.44 micrometers of volume mean particle sizes, and the uniform globular form particles with comparatively narrow particle size distribution of PDI 1.08. The umbrella densities of polymer particles are  $0.25\text{g} / \text{cm}^3$ , They are the porous particles of specific surface area [ of  $9.8\text{m}^2 / \text{g}$  ].

The melting point was 225 \*\*.

[0046](Working example 1)

As an epoxy resin, bisphenol A type epoxy resin (epoxy equivalent 950) 100 weight section, As a hardening agent As trimellitic acid anhydride 8 weight section and a hardening accelerator, bird phenyl phosphine 0.2 weight section, Melting silica powder (average particle diameter of 20 micrometers) 30 weight section and the above-mentioned constituent were blended as porosity polyamide particle 10 weight section obtained by the reference example, and a filler, and it blended by the Henschel mixer, and after carrying out melt kneading in KONIDA, the epoxy resin powdered paint was obtained by grinding. The rate of a flow, thermal shock nature, etc. were measured. A result is shown in Table 1.

[0047](Working example 2) Porosity polyamide particles were replaced with 20 weight sections, and also the epoxy resin granular material constituent was obtained like the working example 1. A result is shown in Table 1.

[0048](Comparative example 1) Made the epoxy resin, the hardening agent, and the hardening accelerator into 100 weight sections, and porosity polyamide particles were not blended, and also it blended like the working example 1, and the epoxy resin constituent was obtained. A



result is shown in Table 1.

[0049](Comparative example 2) It replaced with porosity polyamide particle 90 weight section, and also the epoxy resin constituent was obtained like the working example 1. A result is shown in Table 1.

[0050]

[Table 1]

例		実施例1	実施例2	比較例1	比較例2
ポリアミド含有量	重量%	10	20	0	70
傾斜流動性	単位	11.3	10.4	14.2	5.0
耐熱衝撃性	回数	232	260	25	10
硬度		H	H	H	-

[0051]

[Effect of the Invention] This invention can provide a porosity resin particle restoration epoxy resin constituent. By porosity resin particle restoration, the epoxy resin constituent excellent in destructive intensity, such as thixotropy and thermal shock nature, the impact fracture-proof characteristic, and the crack-proof destructive characteristic, can be provided.

---

[Translation done.]